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Non-Flammable R-410A Alternative for Commercial Refrigeration and Air Conditioning

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ABSTRACT

It is well known that R-410A is the predominant refrigerant used globally in air conditioning systems. However, there has recently been growing interest in R-410A use in commercial refrigeration applications in Japan. Along with the Kigali amendment to the Montreal Protocol to phase down use of HFCs, Japan has enacted HFC regulations with specific GWP limits. For commercial condensing units and larger refrigeration systems, a GWP limit of <1500 GWP will be implemented starting in 2025. To address the need for a lower GWP R-410A alternative, a nonflammable hydrofluoroolefin (HFO) refrigerant mixture named XP41 (R-463A pending) has been developed. XP41 is a five-component mixture of HFO-1234yf with HFC-32, 125, and 134a and a small amount of CO2. HFO-1234yf is included in the formulation to reduce the GWP. HFC-32 and CO2 have been added to increase the cooling capacity and provide comparable performance to R-410A.

For large building air conditioning where variable refrigerant flow (VRF) use is growing, there is also a significant challenge to safely use flammable refrigerants due to large charge sizes. XP41 could potentially address this need as well. This paper will provide detailed information on the properties and other key characteristics of XP41, including drop-in testing in an air conditioning system.

1. INTRODUCTION

There has been growing interest, particularly in Japan to use R-410A in medium and large refrigeration applications. The 100 year GWP of R-410A at 2088 based on the IPCC Fourth Assessment Report (Jallow et. al., 2007) is almost half the GWP of R-404A at 3922. R-410A refrigerating equipment can also be smaller due to its higher capacity, and improved heat transfer properties can result in higher efficiencies.

The GWP of R-410A is still considered to be too high for long-term use and regulations are driving the need to new solutions. In particular, Japan's Ministry of Economic Trade and Industry (METI) has implemented several GWP limits to support goals in the Kigali Amendment to the Montreal Protocol to phase down HFC use (United Nations, 2016). For commercial condensing units and larger refrigeration systems, a GWP limit of <1500 GWP will be implemented in Japan starting in 2025. This will effectively ban the use of R-410A in these systems. However, many commercial refrigeration systems and VRF air conditioning systems have relatively large charge sizes and use of lower GWP flammable refrigerants would be problematic. Therefore, a new solution is needed, as to date there have been no reduced GWP nonflammable alternatives to R-410A proposed.

A new refrigerant, R-463A (pending) has been developed with performance very similar to R-410A. R-463A is a five component mixture of HFO-1234yf with HFC-32, 125, and 134a and a small amount of CO2. HFO-1234yf is in the formulation to dramatically reduce the GWP and HFC-32 and CO2 have been added to increase the cooling capacity and provide performance close to R-410A. The mixture has received a provisional safety classification of A1 nonflammable and low toxicity, and designation R-463A per ASHRAE Standard 34 – Designation and Safety Classification of Refrigerants (ASHRAE, 2016). This included submission of leak and flammability test data to demonstrate nonflammability per ASHRAE 34 and ASTM E681 (ASTM, 2009). R-463A has a GWP of 1494 based on IPCC Fourth Assessment Report which meets the Japan regulatory GWP requirements. It also has a GWP of 1377 based on IPCC Fifth Assessment Report (Myhre et. al., 2013). Several properties of R-463A have been evaluated including thermodynamic refrigeration performance, thermal stability, lubricant miscibility, materials compatibility and electrical properties.

2. THERMOPHYSICAL PROPERTIES AND CYCLE PERFORMANCE

A comparison of thermophysical properties of R-463A compared to R-410A are shown in Table 1. R-463A has a slightly lower boiling point and about 4.5 K higher critical temperature than R-410A. the vapor pressure of R-463A is slightly higher than R-410A due to the lower boiling point. However, liquid densities are very similar indicating system charge sizes should be comparable. The vapor densities of R-463A is slightly lower than R-410A which may reduce mass flow rate.

Table 1: Thermophysical properties

	R-410A	R-463A
Boiling Point, °C	-51.4	-58.5
Critical Point, °C	71.3	75.8
Critical Pressure, °C	4901	5226
Vapor Pressure at 25°C, kPa	1657	1827
Liquid Density at 25°C, kg/m3	1059	1055
Vapor Density at 25°C, kg/m3	66.0	57.8

To evaluate the thermodynamic cooling performance, cycle modeling was performed for R-463A versus R-410A under both medium and low temperature refrigeration conditions: The following conditions were selected to represent medium temperature refrigeration: Evaporator temperature = -10°C, Condenser temperature = 40°C, Subcool amount = 0K, Suction temperature = 10°C and compressor isentropic efficiency = 70%. Cycle modeling results are shown in Table 2.

Table 2: Thermodynamic cycle performance at medium temperature refrigeration conditions

	M_{flow} Rel to R-410A	P_{disch} kPa	P_{disch} Rel to R-410A	T_{disch} °C	CAP kJ/m3	CAP Rel to R-410A	COP	COP Rel to R-410A
R-410A	100%	2393	100%	102	3257	100%	2.59	100%
R-463A	97%	2396	100%	103	3152	97%	2.56	99%

Low temperature refrigeration conditions were also modeled using the following conditions: Evaporator temperature = -35°C, Condenser temperature = 40°C, Subcool amount = 0K, Suction temperature = -15°C and compressor isentropic efficiency = 70%. Results are shown in Table 3.

Table 3: Thermodynamic cycle performance at low temperature refrigeration conditions

	M_{flow} Rel to R-410A	P_{disch} kPa	P_{disch} Rel to R-410A	T_{disch} °C	CAP kJ/m3	CAP Rel to R-410A	COP	COP Rel to R-410A
R-410A	100%	2393	100%	133	1203	100%	1.39	100%
R-463A	93%	2396	100%	132	1115	93%	1.37	99%

R-463A was also modeled at air conditioning conditions using the following conditions: Evaporator midpoint temperature = 10°C, Condenser midpoint temperature = 46.1°C, Subcool amount = 8.3K, Superheat amount = 11.1K and compressor isentropic efficiency = 70%. Results are shown in Table 4.

Table 4: Thermodynamic cycle performance at air conditioning conditions

	M_{flow} Rel to R-410A	P_{disch} kPa	P_{disch} Rel to R-410A	T_{disch} °C	CAP kJ/m3	CAP Rel to R-410A	COP	COP Rel to R-410A
R-410A	100%	2801	100%	82	6782	100%	4.46	100%
R-463A	98%	2783	99%	85	6700	99%	4.45	100%

R-463A exhibits slightly lower pressures and capacity to R-410A however, they are still within 4-7% of R-410A for medium and low temperature refrigeration and within a few percent at air conditioning conditions. The energy efficiency of R-463A is a very close match within 1% of R-410A and compressor discharge temperatures are also similar. The mass flow rate is also within 4-7% or R-410A. Overall, the results indicate there could be potential for use of R-463A in equipment designed for R-410A with minimal modifications.

3. AC SYSTEM PERFORMANCE TESTING

To validate the ideal thermodynamic modeling results, air conditioning system performance has been evaluated in a commercially-available split air conditioning system. Performance was measured in a psychrometric test chamber with an 8.79 kW, 16 SEER ducted split heat pump designed for use with R-410A. The refrigerant charge sizes were determined by optimization of the refrigerant charge to yield the peak energy efficiency in cooling tests. The POE 32 centistoke lubricant used was the same as specified for the compressor with R-410A. Air conditioning tests were done in accordance with ASHRAE Standard 37 and ambient conditions were determined by AHRI 210/240 “B” and “A” cooling conditions, ISO 5151 “T3” conditions, and high ambient “Hot” climate condition commonly used in the AHRI Low-GWP Alternative Refrigerants Evaluation Program (AREP) high ambient temperature testing.

“Drop-in” performance was measured in this system with no modifications to the original equipment except for the addition of measurement instrumentation. The OEM thermostatic expansion valve (TXV) was not adjustable so the amount of superheat measured at the suction of the compressor in the drop-in tests was much lower than for R-410A, at only about 1.2-2.6 K compared to 6.9-11.5 K for R-410A. This helped increase capacity and COP in this case but the much lower amount of superheat near the compressor suction could be a concern for compressor operation. To match the original amount of superheat of the system with R-410A refrigerant, the non-adjustable OEM TXV was then replaced with an adjustable TXV of the same size and capacity and was adjusted to a superheat of about 5.6K (10°R) at the outlet of the evaporator, these results are shown as XP41 (ADJ TXV) in Figures 1-4 below.

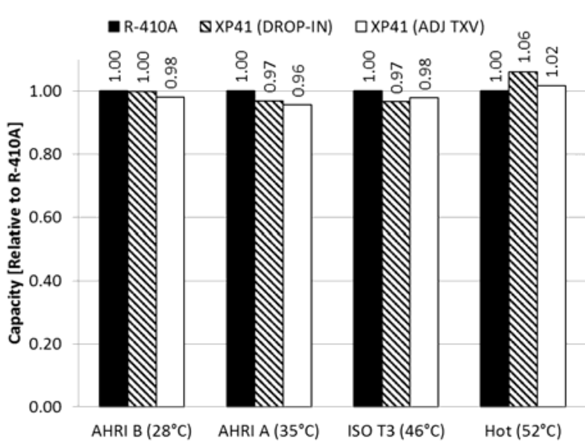

Figure 1: Cooling Capacity Relative to R-410A

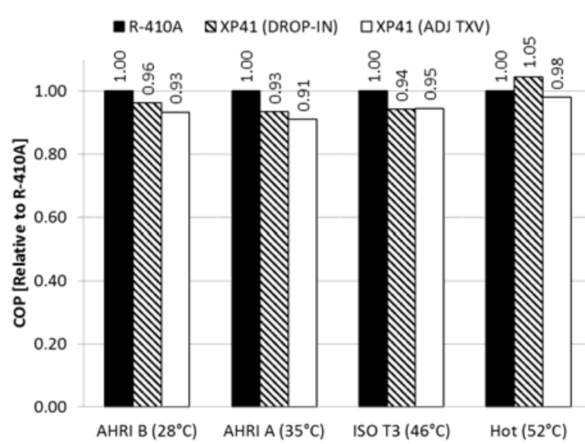

Figure 2: COP Relative to R-410A

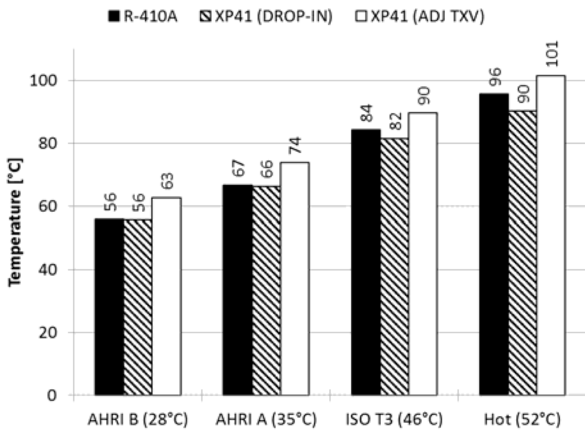

Figure 3: Compressor Discharge Temperature

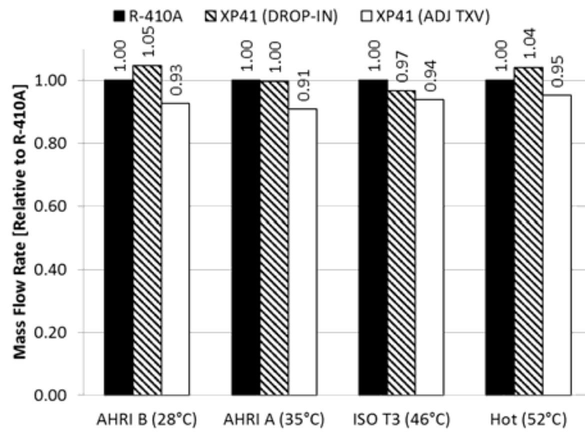

Figure 4: Refrigerant Flow Rate Relative to R-410A

As shown in Figure 1, at the adjusted TXV with equivalent amount of superheat conditions (ADJ TXV) the cooling capacity of XP41 was between 4% lower to 2% higher than R-410A, increasing at the higher ambient temperatures. COP, shown in Figure 2, was between 9% lower to 2% lower than R-410A, also increasing at the higher ambient temperatures. Compressor discharge temperature ranged from about 5-7 degrees Celsius higher than R-410A and refrigerant flow rates were within 9%.

Estimates of the refrigerant charge size based on a thermodynamic properties comparison would suggest that the XP41 refrigerant charge would be within a few percent of the R-410A charge size. However at equivalent charge sizes there was much lower subcooling for R-463A and the charge size that yielded the best energy efficiency in this system was at about 9% higher than R-410A. This is likely an effect of the increased amount of temperature glide in a system with heat exchangers designed for R-410A. The increased refrigerant charge size also led to an increase in the discharge pressures that were higher than the thermodynamic cycle model predicts in Table 4, which would also negatively impact the system COP. Therefore it is expected the capacity and COP could be significantly improved in a system that was optimized for R-463A, including heat exchanger performance that is optimized for the additional temperature glide of R-463A. However the capacity of R-463A was within 4% and COP within 9% even in a system designed for R-410A with minimal modifications, which would suggest there could be potential for use of R-463A in similar applications where R-410A is an acceptable candidate.

4. THERMAL STABILITY

To understand if three were any unique chemical interactions with the components of R-463A thermal stability was evaluated using ASHRAE Standard 97 (ASHRAE, 2007). Two lubricants were used in the study, a polyester (POE) and a polyvinylether (PVE) lubricants. Both lubricants used were nominally 32 centistoke viscosity. Glass tubes were loaded with carbon steel, copper and aluminum coupons. Refrigerant and lubricant were then added to the tubes and frozen before a vacuum was pulled to remove air. In some tubes, air (2000 ppm) contamination was added to refrigerant and moisture contamination (500 ppm) was added to the oil. The tubes were sealed and aged in a heated oven at 175 ^{o}C for 14 days. Tubes and coupons were visually inspected and contents analyzed after exposure for fluoride ion using ion chromatography. High concentrations of fluoride ion would indicate fluid decomposition. MDL (Minimum Detection Limit) indicates fluoride ion level was below the procedure detection limit of (MDL = 0.3 ppm). As shown in Table 4, R-463A was determined to be thermally stable as negligible amounts of fluoride ion were generated and metal coupons and fluids showed no visible changes.

Table 5: Thermal Stability Results

Refrig/Oil	Air (ppm)	Water (ppm)	F- Ion (ppm)	Visual Inspection
R-463A/POE	None	None	<MDL	No change
“	None	500	7.7	No change

“	2000	None	6.4	No change
“	2000	500	<MDL	No change
R-463A/PVE	None	None	<MDL	No change
“	None	500	<MDL	No change
“	2000	None	<MDL	No change
“	2000	500	<MDL	No change

5. LUBRICANT MISCIBILITY

The miscibility of R-463A was tested with a POE 32 and PVE 32 centistoke lubricant. A range of refrigerant and oil mixture compositions were prepared in sealed glass tubes. The tubes were heated to 70°C and then cooled to -50°C and observed in 5K increments. Results are show in Table 5 and 6. R-463A shows excellent miscibility with very small immiscible regions. Therefore, R-463A is expected to be suitable for use with POE and PVE lubricants in the operating ranges of commercial refrigeration systems.

Table 6: Miscibility of R-463A with POE Lubricant

							Temperature				(deg C)														
refrig/ oil (wt%)	**-50**	**-45**	**-40**	**-35**	**-30**	**-25**	**-20**	**-15**	**-10**	**-5**	**0**	**5**	**10**	**15**	**20**	**25**	**30**	**35**	**40**	**45**	**50**	**55**	**60**	**65**	**70**
95 / 5%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
90 / 10%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	I	I
85 / 15%	I	I	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	I	I	I
80 / 20 %	I	I	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	I	I	I	I
70 / 30%	I	I	I	I	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	I	I	I
40 / 60%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
30 / 70%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M

Table 7: Miscibility of R-463A with PVE Lubricant

							Temperature				(deg C)														
refrig/ oil (wt%)	**-50**	**-45**	**-40**	**-35**	**-30**	**-25**	**-20**	**-15**	**-10**	**-5**	**0**	**5**	**10**	**15**	**20**	**25**	**30**	**35**	**40**	**45**	**50**	**55**	**60**	**65**	**70**
95 / 5%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
90 / 10%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	I	I
85 / 15%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	I	I
80 / 20 %	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	I	I	I
70 / 30%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	I	I
40 / 60%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
30 / 70%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M

6. PLASTICS AND ELASTOMERS COMPATIBILITY

The compatibility of R-463A was evaluated with a range of typical plastics and elastomers typically used in the refrigeration industry. Samples of different plastics and elastomers were prepared and their initial weights and dimensions measured. Samples were then placed in sealed glass tubes which were loaded with a 50/50 mixture of refrigerant and POE 32 or PVE 32 lubricant. The tubes were filled and placed in a 100 °C oven for two weeks. After heating, the plastics were removed and measured for changes in physical properties (weight, length, and hardness change) twenty four hours after removal from the tubes. The following rating system was used to characterize the compatibility of the different samples tested:

0 = <10% weight change and <10% linear swell and <10 hardness change

1 = >10% weight change or >10% lineal swell or 10 hardness change
2 = >10% weight change and >10% linear swell and >10 hardness change

Compatibility results for POE are sown in Tables 7-8 and for PVE in Tables 9-10. Ratings for most plastics and elastomers were excellent demonstrating minimal changes after exposure. Overall, the plastics showed less reactivity than the elastomers which is typical of refrigerant compatibility testing. It should be recognized that these data reflect compatibility in sealed tube tests, and that refrigerant compatibility in real systems can be influenced by the actual operating conditions, the nature of the polymers used, compounding formulations of the polymers, and the curing or vulcanization processes used to create the polymer. Specific grades, additives, etc. can also vary and potentially affect results for different polymers and other materials.

Table 8: Plastics Compatibility of R-463A and POE 32

R-463A + POE 32	Rating	% Weight Change	% Linear Swell	Hardness Change, Delta
Polyester	0	9	3	-1
Nylon resin	0	0	3	-3
Polyamide-imide	0	0	0	-1
Polyphenylene sulfide	0	0	0	0
PEEK	0	1	0	-1
Nylon	0	1	0	0
PTFE	0	1	0	0

Table 9: Elastomers Compatibility of R-463A and POE 32

R-463A + POE 32	Rating	% Weight Change	% Linear Swell	Hardness Change, Delta
Neoprene	0	3	1	-4
Epichlorohydrin	1	7	3	-14
Butyl Rubber	0	9	3	-9
EPDM	0	6	2	-8
Fluorosilicone	0	5	2	-10
HNBR	1	16	5	-8
NBR	1	13	4	-12
Fluorocarbon FKM	1	15	7	-13
Viton A	1	15	6	-13
Viton GF	0	9	4	-9

Table 10: Plastics Compatibility of R-463A and PVE 32

R-463A + PVE 32	**Rating**	**% Weight Change**	**% Linear Swell**	**Hardness Change, Delta**
Polyester	0	7	2	0
Nylon resin	0	0	3	-6
Polyamide-imide	0	0	0	0
Polyphenylene sulfide	0	0	0	0
PEEK	0	1	0	0
Nylon	0	1	0	0
PTFE	0	2	1	-1

Table 11: Elastomers Compatibility of R-463A and PVE 32

R-463A + PVE 32	**Rating**	**% Weight Change**	**% Linear Swell**	**Hardness Change, Delta**
Neoprene	0	0	0	4
Epichlorohydrin	0	4	2	-2
Butyl Rubber	1	10	3	-8
EPDM	0	7	2	-8
Fluorosilicone	0	3	1	-3
HNBR	0	9	3	-4
NBR	0	6	1	-7
Fluorocarbon FKM	0	8	4	-9
Viton A	0	9	3	-9
Viton GF	1	8	3	-11

7. DIELECTRIC PROPERTIES

Dielectric properties are important to understand for refrigeration systems using hermetic motors. It has been widely adopted to use Oster's mixing rule for the polarizability of regular mixtures, when only pure component values are known. In the limit of zero excess volume, the mixing rule reduces to a volumetric average for the mixture polarizability (Harvey & Lemmon, 2005). The dielectric constant was then calculated using the Kirkwood approximation for polarizability of polar compounds (Wang and Anderko, 2001). In the current model, a single mixing parameter is used to account for deviations from regular solution behavior. Results are shown in Table 12. Our previous work (Minor et al. *pending*) has cited Gbur (2005) for the experimental static dielectric constant value of liquid R-410A at 25 °C, its value being considerably smaller than a previous measurement by Pietsch (1998), as shown in Table 12. Since then, a more recent publication (Mazza & Marcela, 2016) was found in the literature. It reports experimental liquid dielectric constant values of R-410A as a function of temperature, the value at 25 °C being larger and more consistent with other HFC blends literature values. Therefore, the mixing rule parameter has been since re-fit to account for this new data, using experimental pure component static dielectric constants for R-1234yf, R-32, R-125 and R-134a (Gbur, 2005; Sedrez and Barbosa, 2014). From Table 12, we see that the calculated values for the incumbent fluid, R-410A, as well as an HFC blend that also contains R-32, R-407C, are reasonable compared to literature experimental values, which lends credibility to the R-463A calculation.

Table 12: Dielectric Constants at 25°C

Refrigerant	**Determination**	**Dielectric Constant Saturated Liquid**	**Dielectric Constant Saturated Vapor**
R-410A	Experimental (Gbur, 2005)	5.4	1.18
R-410A	Experimental (Pietsch, 1998)	7.8	-
R-410A	Experimental (Mazza & Marcela, 2016)	8.9	-
R-410A	Calculated	9.8	1.13
R-407C	Experimental (Gbur, 2005)	10.2	1.09
R-407C	Experimental (Pietsch, 1998)	8.7	-
R-407C	Calculated	9.74	1.13
R-463A	Calculated	12.8	1.19

8. CONCLUSIONS

A new nonflammable HFO-based refrigerant R-463A has been developed as a potential replacement for R-410A in commercial refrigeration and air conditioning. It meets the regulatory requirements in Japan implementing a <1500 GWP cap in commercial refrigeration. Thermophysical properties, thermodynamic cycle performance, and air conditioning system tests demonstrate it is a close capacity and COP match to R-410A in commercial refrigeration and air conditioning applications. Thermal stability, lubricant miscibility, plastics and elastomers compatibility and dielectric properties demonstrate R-463A is a suitable replacement for R-410A. Use of R-463A can reduce the environmental impact of refrigeration systems by allowing transition away from R-410A with a refrigerant with similar performance and properties.

NOMENCLATURE

ASHRAE	American Society of Heating, Refrigerating and Air Conditioning Engineers	
CAP	volumetric cooling capacity	(Btu/ft^3, kJ/m^3)
COP	coefficient of performance	
EPDM	ethylene propylene diene terpolymer	
GWP	global warming potential	
HNBR	hydrogenated nitrile butadiene rubber	
IPCC	Intergovernmental Panel on Climate Change	
METI	Ministry of Economy, Trade and Industry	
M_{flow}	mass flow rate	(lb/hr, kg/hr)
MDL	minimum detection limit	(ppm)
NBR	nitrile butadiene rubber	
Pdisch	compressor discharge pressure	(psia, kPa)
PEEK	polyether ether ketone	
POE	polyol ester lubricant	
P	pressure	(psia, kPa)
PTFE	polytetrafluoroethylene	
PVE	polyvinylether	
T	temperature	(°F, °C)
Tdisch	compressor discharge temperature	(°F, °C)

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